THERMOCHEMISTRY OF BROMOCOMPLEXES OF THIRD ROW TRANSITION ELEMENTS

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ABSTRACT

The enthalpy of the process $2RbBr(c) + TaBr_4(c) = Rb_2TaBr_6(c)$ has been determined by solution calorimetry. The standard enthalpy of formation of Rb_2TaBr_6 was found to be -316.6 kcal mol^{-1}. Based upon a Kapustinskii calculation of lattice energy, the standard enthalpy of formation of $TaBr_6^{2-}$ (g) was found to be -194.4 kcal mol^{-1}. The double bromide affinity of $TaBr_4$(g) and the lattice energy of Rb_2TaBr_6(c) were compared with values of corresponding compounds of Ti, Zr, Hf, W, Re and Pt.

INTRODUCTION

In previous work [1–5] we have determined the enthalpies of formation of a series of alkali hexachloro- and hexabromometallates with central atoms in the +4 oxidation state. The values were derived from solution calorimetric studies of the processes

$$2AX(c) + MX_4(c) \rightarrow A_2MX_6(c) \qquad (1)$$

where A = Na, K, Rb or Cs. In those cases in which the necessary ancillary data are available, we derived the double halide ion affinities, represented by the enthalpy of reaction (2).

$$MX_4(g) + 2X^-(g) \rightarrow MX_6^{2-}(g) \qquad (2)$$

Jenkins and Pratt have reviewed the existing data for this type of process [6,7].

Data for chloride systems are fairly extensive, but they are scarce for bromides. By reporting the enthalpy of formation of an alkali hexabromo-tantalate(IV) in the present work, we have been able to complete the third transition series from Group IV to Group VII, inclusive.

EXPERIMENTAL

Preparation of materials

The preparation of $TaBr_4$ was as described previously [8]. Analysis: calcd. for $TaBr_4$: Br, 63.86%; found: Br, 63.41%. The salts Rb_2TaBr_6 and Cs_2TaBr_6 were prepared following the method of Torp [9] by melting a stoichiometric mixture of $TaBr_4$ and alkali bromide in sealed, evacuated quartz ampoules. The caesium salt was not sufficiently soluble for study by solution calorimetry. Analysis: calcd. for Rb_2TaBr_6: Br, 57.67%; found: Br, 57.45%. The compounds were handled in a dry nitrogen atmosphere and stored in sealed ampoules.

Calorimeter

The calorimeter and the methods of manipulation of samples have been described previously [8]. The calorimeter liquid was $7.80 \pm 0.02\%$ (w/w) hydrofluoric acid that was prepared from 48% acid (Baker). The concentration was verified by titration. Argon was used to purge solutions of oxygen in the calorimeter. Failure to do so led to oxidation of Ta(IV) by air rather than by the solvent acid (as required by eqn. (4) below). One hour was allowed for out-gassing and the argon flow was reduced to 5 ml min^{-1} just prior to the commencement of a run. The argon was passed through a copper coil immersed in a thermostat bath held at 25°C.

RESULTS AND DISCUSSION

Most of the thermochemical data for alkali hexahalometallates have been obtained for salts with the potassium chloroplatinate structure ($Fm3m$, O_h^5). Comparisons between various systems are facilitated if all the salts under study have the same structure. The alkali bromotantalates(IV) with this structure are Rb_2TaBr_6 and Cs_2TaBr_6. The latter is unsuitable for calorimetry as it is not readily soluble. K_2TaBr_6 has a tetragonal unit cell.
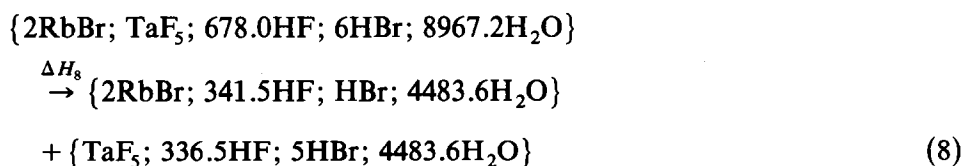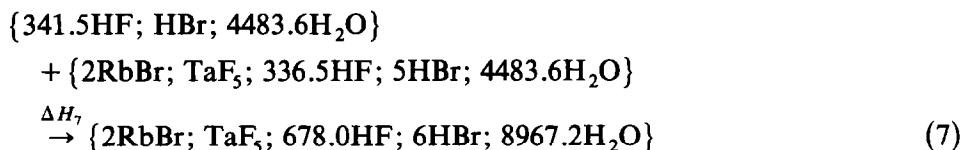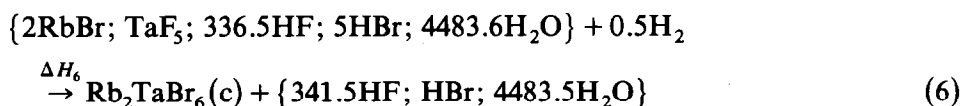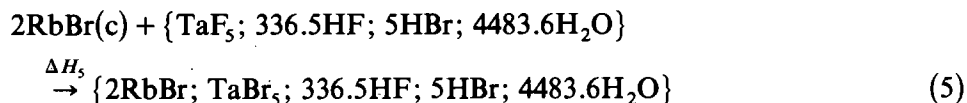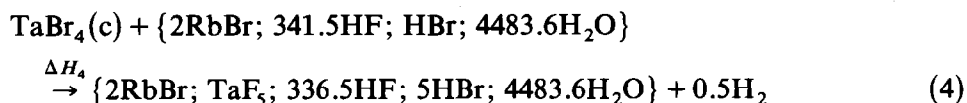
The enthalpy of complexing for Rb_2TaBr_6 was determined by measuring the enthalpies of solution of each of the compounds in eqn. (3).

$$2RbBr(c) + TaBr_4(c) \rightarrow Rb_2TaBr_6(c) \qquad (3)$$

Tantalum(IV) salts are rapidly converted to fluorotantalate(V) in hydrofluoric acid solution along with the evolution of hydrogen. We therefore assumed that Rb_2TaBr_6 dissolved in hydrofluoric acid solution to give the same species as were formed when $TaBr_4$ and RbBr were dissolved separately.

Partial reactions (4)–(8) were used to calculate heats of complexing. Braces denote solution components and the number of moles for each

component refer to the typical case in which 2 g of $TaBr_4$ were dissolved in 350 g of 7.80% (w/w) HF solution. The reactions are written for one mole of tantalum compound. The 350-g portions of acid used in the calorimeter contained 1.364 mol HF and 17.91 mol H_2O. The acid concentration was chosen to conform to that used in a previous research [8].

$$TaBr_4(c) + \{2RbBr; 341.5HF; HBr; 4483.6H_2O\}$$

$$\xrightarrow{\Delta H_4} \{2RbBr; TaF_5; 336.5HF; 5HBr; 4483.6H_2O\} + 0.5H_2 \tag{4}$$

$$2RbBr(c) + \{TaF_5; 336.5HF; 5HBr; 4483.6H_2O\}$$

$$\xrightarrow{\Delta H_5} \{2RbBr; TaBr_5; 336.5HF; 5HBr; 4483.6H_2O\} \tag{5}$$

$$\{2RbBr; TaF_5; 336.5HF; 5HBr; 4483.6H_2O\} + 0.5H_2$$

$$\xrightarrow{\Delta H_6} Rb_2TaBr_6(c) + \{341.5HF; HBr; 4483.5H_2O\} \tag{6}$$

$$\{341.5HF; HBr; 4483.6H_2O\}$$
$$+ \{2RbBr; TaF_5; 336.5HF; 5HBr; 4483.6H_2O\}$$

$$\xrightarrow{\Delta H_7} \{2RbBr; TaF_5; 678.0HF; 6HBr; 8967.2H_2O\} \tag{7}$$

$$\{2RbBr; TaF_5; 678.0HF; 6HBr; 8967.2H_2O\}$$

$$\xrightarrow{\Delta H_8} \{2RbBr; 341.5HF; HBr; 4483.6H_2O\}$$

$$+ \{TaF_5; 336.5HF; 5HBr; 4483.6H_2O\} \tag{8}$$

Process (4): the dissolving of $TaBr_4$ in 7.80% hydrofluoric acid

Process (4) requires that 2.0 g of $TaBr_4$ be dissolved in 350 g of 7.80% HF which also contains 1 mol HBr per mole of $TaBr_4$ employed. The requisite amount of HBr was added to the calorimeter acid in the form of an aqueous solution. The resulting slight change in the concentration of HF was compensated for by using a slightly more concentrated HF solution. In the absence of such compensation the resulting error was shown to be ± 0.05 kcal mol^{-1}. It was not convenient to prepare exactly 2.0-g samples of $TaBr_4$ as indicated by the ideal partial process (4). Instead, various quantities were dissolved in 7.80% hydrofluoric acid and the mean value of the observed enthalpies was chosen. There was no indication that the enthalpy of solution was influenced by sample size.

The reaction produced 0.5 mol H_2 per mole of $TaBr_4$ dissolved. The gas evolved was saturated with water vapour. According to the vapour pressure data of Brosheer et al. [10], 0.014 mol water was thereby removed from the solution which therefore entailed a correction of -0.15 kcal mol^{-1} $TaBr_4$.

The value of ΔH_4 was obtained in a previous research [8] and, including the correction for water evaporation, was found to be -82.3 ± 0.5 kcal mol^{-1}. The uncertainty limits here, and below, indicate the standard deviation of the individual values from the mean value.

Process (5): the dissolving of RbBr in 7.80% hydrofluoric acid

As in previous work of this kind, the enthalpy of dissolving RbBr in the calorimeter solution was essentially independent of the size of the sample taken. The values of ΔH_5 found were 7.94, 7.98, 7.82 and 7.54 kcal per two moles of RbBr. Mean value: 7.82 ± 0.18 kcal mol^{-1}.

Process (6): the dissolving of Rb_2TaBr_6 in 7.80% hydrofluoric acid

Process (6) was run in the reverse direction by dissolving Rb_2TaBr_6. This resulted in hydrogen evolution in the same way as Process (5) and the same precautions of purging with argon and correcting for evaporation were applied. The corrected values obtained for ΔH_6 were 69.51, 69.62, 69.59, 69.50 and 69.69 kcal mol^{-1}. Mean value: 69.56 ± 0.06 kcal mol^{-1}.

Processes (7) and (8): the mixing of acid solutions

Process (7) is essentially the further dilution of a dilute solution of RbBr, TaF$_5$ and HF to twice the volume. Standard Tables [11] show that the enthalpy effects for the RbBr and HF solutes are of the order of a few hundredths of a kilocalorie per mole of Ta. Process (8) is similar, but in the reverse direction. The sum of the enthalpies of Processes (7) and (8) is clearly quite negligible.

The sum of the enthalpies of Processes (4)–(8) is that of eqn. (3): $\Delta H_3 = -5.0 \pm 0.5$ kcal mol^{-1}. The compound is only marginally stable.

The standard enthalpies of formation of crystalline Rb_2TaBr_6 and gaseous $TaBr_6^{2-}$ are found to be

$$\Delta H_f^0(Rb_2TaBr_6)(c) = -316.6 \text{ kcal mol}^{-1}$$

$$\Delta H_f^0(TaBr_6^{2-})(g) = -194.4 \text{ kcal mol}^{-1}$$

The value for the ion depends upon a calculation of the lattice energy of Rb_2TaBr_6. This followed the method of Kapustinskii [12] and gave the value 358.8 kcal mol^{-1}. Torp's value of the lattice constant, $a = 10.62$ Å, was used [9]. The following enthalpies of formation were also used (kcal mol^{-1}): RbBr(c), -93.0 [10]; TaBr$_4$(c), -125.6 [8]; Rb$^+$, -118.3 [10].

Lattice energies calculated by the Kapustinskii method [12] are not accurate as the anionic groups are treated as point charges. A superior approach is that of Jenkins and Pratt [13] but their procedure requires a

TABLE 1

`Double bromide affinities (kcal mol^{-1})

HfBr$_4$	+13	ReBr$_4$	+40
TaBr$_4$	+43	PtBr$_4$	+26 [a]
WBr$_4$	+45		

[a] We consider ΔH_f^0 for K$_2$PtBr$_6$ suspect: see the discussion of the data plotted in Fig. 1.

knowledge of metal–halogen distances and the partial charges on the atoms. The cruder calculation allows comparison of results for closely related compounds such as A$_2$ZrBr$_6$ and A$_2$WBr$_6$.

Enthalpies for Process (2) cannot be calculated for TaBr$_4$, WBr$_4$ and ReBr$_4$ owing to the unavailability of their respective enthalpies of sublimation. Jenkins and Pratt have defined $\Delta \overline{H}_{Br}(c)$ as the enthalpy of Process (9)

$$MBr_4(c) + 2Br^-(g) \rightarrow MBr_6^{2-}(g) \qquad (9)$$

which is the next best alternative for comparison. The values in Table 1 show no particular trend of bromide affinity in the period, unlike the trend which has been observed in chloro systems of the second and third periods [6,7]. The situation appears to be very different with actinides, however, where UBr$_4$ exhibits a much greater affinity for bromide than does ThBr$_4$ [5]. Because the lattice energies are very uncertain, trends in double halide affinities are qualitative at best. The reliability of the measured data can be tested by a device outlined in a previous publication [14]. Values of $-\Delta H_f^0 + S + \Sigma I$ for bromocomplexes, plotted against values for corresponding chlorocomplexes, should give an essentially straight line. S and ΣI are enthalpies of sublimation and ionization of the transition metal, respectively. For all of the transition elements shown in the plot (Fig. 1), except Ti, Zr and Hf, the values of the third and fourth ionization potentials were estimated by extrapolations of the available data. This leads to rather uncertain values of ΣI, especially for Pt, but this is of no consequence for the linearity in the present instance because the slope of the line is, fortuitously, unity. The relative displacements along the line are affected by errors in ΣI, however.

The plotted data, with the exception of the point for K$_2$PtX$_6$, are self-consistent, demonstrating the uniformity of trends in the behaviour of the elements under study. We consider the thermal data for K$_2$PtX$_6$ to be suspect. Thermal data, when not our own, were taken from ref. 6.

If the lattice energies * are primarily electrostatic, the slope of the line

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* The energies referred to are for the process A$_2$MX$_6 \rightarrow 2A^+ + M^{4+} + 6X^-$.
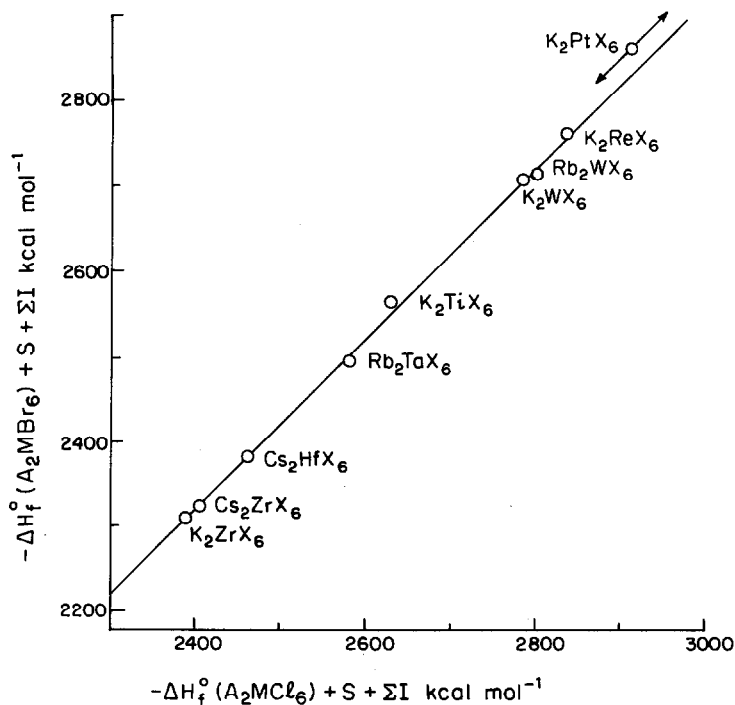
Fig. 1. Plot of the lattice energy function $-\Delta H_f^0 + S + \Sigma I$ for various salts: A_2MX_6.

should be given by

$$\frac{d(r_c + r_{Br^-})^{-1}}{d(r_c + r_{Cl^-})^{-1}} = \frac{(r_c + r_{Cl^-})^2}{(r_c + r_{Br^-})^2}$$

The observed slope is, however, close to 1.0, i.e., it is greater than that for a purely electrostatic system. This indicates that, as lattice energy increases along the series of compounds, the bromocomplexes gain in stability at a faster rate than do the chlorocomplexes. This points out the importance of polarization or π-bonding in the case of the heavier halogens.

For compounds containing a specific alkali element, e.g., the compounds K_2MX_6, the relative positions along the plot provide a comparison of the heterolytic bond energies of the MX_6^{2-} groups. As stated above, errors in ΣI values also affect the positions. It is apparent that the bond energies generally increase across a period. This was deduced previously by Jenkins and Pratt [6] who employed an approach involving the calculation of lattice energies. We differ from them regarding the positions of elements in the higher periods (Ti and Zr) relative to elements in the third transition period.

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